BACKGROUND CONCENTATIONS OF SELECTED CHLORINATED HYDROCARBONS IN RESIDENTIAL INDOOR AIR

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ABSTRACT
Groundwater plumes containing volatile organic compounds are a potential source of organic vapors in indoor air. At the same time, many household products and building materials are known to be sources of background VOCs in indoor air. More than 2000 pre- and post-remediation indoor air samples have been collected in residences at a site in Denver, Colorado. These were collected over 24-hours in passivated SUMMA canisters and analyzed by EPA Method TO-14/15 using part per trillion detection limits. An evaluation of background concentrations of 8 chlorinated VOCs in this database was performed. The data were screened to exclude site-impacted results by evaluating VOCs in homes with vapor intrusion mitigation systems that successfully reduced concentrations of the principle groundwater contaminant, 1,1-DCE, by up to three orders of magnitude. Based on over 280 background residential indoor air samples from nearly 100 residences, the results provide well-characterized background concentrations for these chlorinated hydrocarbons.

INDEX TERMS
Background, chlorinated VOCs, residential

INTRODUCTION
The subsurface vapor intrusion to indoor air pathway is becoming widely recognized as a potentially significant pathway for long-term exposure to volatile organic compounds (VOCs) (Folkes & Kurz, 2000; Johnson, et. al., 2001). An essential part of the evaluation of this pathway is the quantification of "background" indoor air VOC concentrations (i.e. indoor air impacted by all other sources) so that "incremental risk" from subsurface vapor intrusion to indoor air can be quantified. These "background" indoor air VOC concentrations are caused by typical consumer products (Wallace, et.al, 1987, Tichenor and Mason, 1988, Sack, et.al., 1992), as well as building materials and ambient air.

Few published studies are available on background concentrations of the full TO15 suite of chlorinated VOCs in residential indoor air. However, it is widely recognized (USEPA, 1987) that residential indoor air sources of some of these VOCs can be quite significant (especially methylene chloride (DCM) from paint products and tetrachloroethene (PCE) from dry cleaning).

In the process of characterizing a vapor intrusion site in the Denver area (Redfield Rifle Scope), an opportunity arose to characterize background chlorinated VOCs in a large number of residences using modern, low detection limit methods (TO15) and 24-hour SUMMA canister sampling. The Redfield data was collected from mid 1998 to December 14, 2001

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from several hundred single family homes, including nearly 300 homes with radon-type remediation systems installed to reduce or eliminate levels of 1,1-DCE due to vapor intrusion.

Of the 50 volatile organic compounds typically analyzed by EPA Method TO-15, only six are potentially groundwater-derived Chemicals of Concern (COCs) at the site (1,1,1-trichloroethane (1,1,1-TCA); 1,1-dichloroethane (1,1-DCA); 1,1-dichloroethylene (1,1-DCE); trichloroethylene (TCE); PCE; and vinyl chloride). Two additional compounds were included in the routine SIM mode indoor air analyses at this site (DCM and 1,2-DCA). The 1,1-DCE concentrations measured were conservatively assumed to be derived totally from vapor intrusion. Therefore, 1,1-DCE was used to screen the total database for only those samples with non-detectable DCE.

Previous Work

A number of studies have been published in recent years dealing specifically with background chlorinated VOCs in indoor air (Samet, et.al, 1987; Wallace, et.al, 1987; Tichenor and Mason, 1988; Sheldon, 1991; Sack, et.al, 1992; Wallace, 1995; Roberts and Dickey, 1995; Davis and Otson, 1996; Ott and Roberts, 1998). In general, all of these studies have found 1,1,1-TCA, TCE, PCE, Benzene, DCM and Chloroform to be commonly present in residential indoor air, even at rural locations far removed from industrial sources. However, very few published studies have had adequately low detection limits to detect the presence of 1,1-DCE, 1,2-DCA or Vinyl Chloride in background indoor air. A few studies identified the presence of 1,1-DCE, but with very poor quantification of the levels found.

Ott & Roberts (1998), found that the concentrations of 11 volatile organic compounds (TCE; 1,1,1-TCA; xylenes; benzene; ethylbenzene; PCE; m- & p-dichlorobenzene; chloroform; and styrene) were much higher indoors than outdoors in two New Jersey cities with numerous chemical processing plants. In this situation it was expected that outdoor air would be more contaminated than indoor air due to industrial air emissions. Average indoor concentrations of PCE were more than twice those of outdoor air. They also noted that the major source of exposure to chloroform is from chlorinated water supplies.

In summary, literature data is fairly consistent in reporting the common occurrence of elevated levels of 1,1,1-TCA, TCE, DCM, PCE, benzene and chloroform in residential indoor air due to indoor sources of these chemicals. However, very limited reliable data exist for the abundance of 1,1-DCA, 1,2-DCA, 1,1-DCE and vinyl chloride in residential indoor air.

SAMPLING AND ANALYTICAL METHODS

All indoor samples were collected over a 24-hour time period with passivated 6-liter SUMMA canisters dedicated to the specific project. Samples were typically collected on a quarterly basis in the lowest potential living space of a residence, regardless of occupancy. Samples were analyzed for 8 compounds at both Quanterra (Severn Trent) and Advanced Technology Laboratories by EPA methods TO-15 in selective ion monitoring mode (SIM). Method detection limits were determined according to EPA protocols. The SIM reporting limits for the Redfield site are provided in Table 1.

STATISTICAL METHODS

For all of the Redfield SIM data, non-detects at the reporting limit were assigned a value equal to one half the reporting limit. Post-remediation SIM results with DCE greater than the reporting limit (0.04 ug/m3) were screened out of the Redfield background data. This

screening was done to exclude any data that may have been impacted by vapor intrusion. DCE was chosen for the screening because it has the lowest detection limit of the COCs, the highest volatility, as well as the highest concentration in groundwater and impacted indoor air at the site. DCE is also likely to have the lowest background concentration because it is generally not available commercially, although it may be present as an impurity in products containing TCA or TCE (Stewart, et.al, 1969) and historically was known to be present in plastic food wrap, flame retardant fabrics, carpet backing and adhesives. Due to the relative detection limits of the COCs and relative volatilities, if DCE is below detection, none of the other COCs could be present in measurable concentrations if derived from vapor intrusion. The resulting post remediation "background" data set of 282 samples contains indoor air data from 120 homes at the site.

BACKGROUND POPULATION DISTRIBUTIONS

The remaining data, after the above processing, were analyzed by probability plotting methods to determine the most appropriate type of population distribution. The majority of the chemicals correspond to log normal population distributions, although outliers are evident (Fig. 1). DCM shows anomalous behavior with several apparent populations indicated by the segments on the log probability plot with different slopes. This multiple population character is consistent with, and could be attributed to, the prevalence of DCM in numerous consumer products.

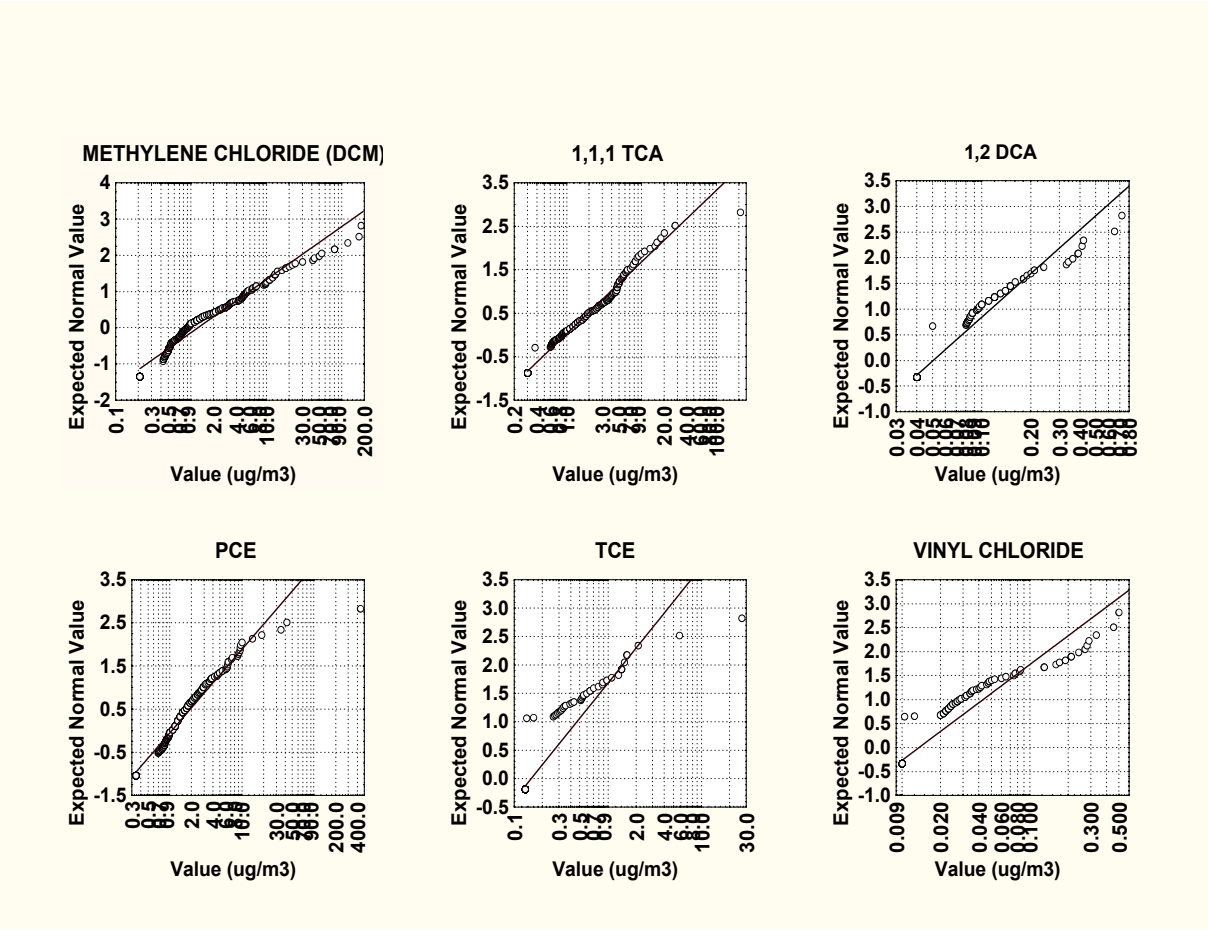

Figure 1. Log Probability Plots

After determination of the population distribution, all data were log normalized. Dixon's Test (Dixon, 1953) was used to screen the log normalized indoor data for individual outliers.

Data determined to be outliers at the 95% confidence level were excluded from further analysis. Only two outliers were removed from the background data set composed of over 282 samples. The complete analysis for an outlier sample was removed. Outliers, or extreme values, are noted for DCM, PCE and 1,1,1-TCA. Outliers are thought to be due to unusual consumer product usage and potentially, rare analytical errors.

BACKGROUND INDOOR AIR RESULTS

There are a large number of VOCs, including chlorinated compounds, commonly present at detectable levels in background indoor air at the site. DCM, PCE, and 1,1,1-TCA were detected the most frequently, followed by vinyl chloride, 1,2-DCA, and TCE (Table 1). The lower detection limits for vinyl chloride and 1,2-DCA may explain, at least in part, their more frequent detection compared to TCE. The median concentrations for DCM, PCE, 1,1,1-TCA are similar and in the range of 0.9 to 1 ug/m^3. Maximum values for all compounds are significantly higher than the medians, and over 2 orders of magnitude higher for DCM, PCE, and 1,1,1-TCA. Detected DCM, PCE, and 1,1,1-TCA concentrations range over approximately 3 orders of magnitude. The other VOCs ranged over approximately 1 order of magnitude, but this range is likely truncated by the detection limits.

Table 1. Summary statistics for post remediation background indoor air

	Valid	Reporting	Detection		Geometric	95UCL	Max.	Percentiles	
Compound	N	Limit	Frequency	Median	Mean	ug/m^3	ug/m^3	90th	95th
DCM	282	0.42	82.3%	0.88	1.28	4.46	180	10	16
1,1DCA	282	0.08	0.71%	<0.08	<0.08	<0.08	0.16		<0.08
1,1DCE	282	0.04	0%	<0.04	<0.04	<0.04	<0.04		<0.04
1,1,1TCA	282	0.6	61.0%	0.86	1.03	2.53	210	5.1	7.8
1,2DCA	282	0.08	24.8%	0.04	0.054	0.068	0.72	0.1	0.18
PCE	282	0.68	69.9%	1	1.12	2.23	440	4.5	6.5
TCE	282	0.26	13.8%	0.13	0.164	0.224	27	0.3	0.7
Vinyl chloride	282	0.02	25.2%	0.01	0.015	0.023	0.5	0	0.09

SOURCES OF VARIABILITY

There are numerous sources of variability for indoor air data. These include laboratory precision and blank, field sampling procedures, seasonal influences due to varying air exchange rates and variable product use by and between residents.

Lab replicates for SIM compounds routinely show a Relative Percent Difference (RPD) of less than 10% (Coefficient of Variation (COV) = 5%). Field duplicates typically show variability of less than 50% RPD (COV=25%), however differences in concentration of a single SIM compound have been found to occasionally range up to a factor of six.

Over a period of several years, the variability in background indoor air concentrations within an individual residence is typically within a factor of five (Coefficient of Variation =30 to 50 %). The compound showing the greatest variability is PCE, frequently showing a COV of greater than 100%. The compound 1,2-DCA generally shows the lowest variability within a residence (typically within a factor of three).

The variability in background indoor air concentrations between residences on a site is typically within an order of magnitude. The compound showing the greatest variability is PCE. For this compound the residence to residence means vary by a factor of 15 to 20. The compound showing the least variability (most consistent across residences) is 1,2-DCA. For this compound the residence to residence means vary by a factor of five to eight. For an individual compound, the COV seems to be fairly consistent across residences, regardless of the mean concentration, indicating a constant variance.

In one case on the site, an extreme concentration of 1,1,1-TCA (460 ug/m^3), unrelated to groundwater contamination, is associated with significant concentrations of 1,1-DCA, 1,1-DCE and 1,2-DCA. In this case, it appears that these three compounds are present as impurities or breakdown products of a consumer product rich in 1,1,1-TCA (Henschler, et.al., 1980).

CONCLUSIONS

A large number of volatile organic compounds are found consistently in residential indoor air due to indoor or ambient air sources. This report demonstrates that at least 6 chlorinated compounds are also commonly present. A number of these compounds (1,2-DCA; methylene chloride; PCE; TCE) are found at concentrations that exceed EPA screening levels.

These compounds are generally present at higher concentrations than in the local & regional outdoor air, consistent with findings in the literature (Ott & Roberts, 1998).

The present study provides reliable, low-detection limit background indoor air data for a number of compounds, including: 1,1-DCA; 1,2-DCA; and vinyl chloride. The results for vinyl chloride show a significant percentage of detections in the concentration range of 0.02 to 0.5 ug/m^3. Clearly, detectable concentrations of vinyl chloride can arise in indoor air from indoor sources. Similarly, 1,2-DCA shows a high percentage of detections in the range of 0.08 to 0.72 ug/m^3.

For the remaining compounds, concentrations in typical indoor air in this part of Denver are generally at the low end of mean indoor air concentrations previously reported for residential settings. They are most similar to those reported for rural and small urban environments. This observation is likely to be due to two effects. First, most previous literature data utilized higher detection limit methods and secondly, the present results may be biased low due to the high public awareness of indoor air issues at the site (see Cautionary Note).

The results of the Redfield study clearly indicate the importance of residential surveys and inspections as part of any indoor air site investigation. Attached garages, solvent/paint/adhesive storage and other consumer products can have large impacts on indoor air measurements for many chlorinated VOCs.

Cautionary Notes:

In a number of cases, residents have been advised to avoid cleaning prior to sampling, to avoid hobbies that utilize VOCs, and to remove VOC-containing materials from their basements and garages. Because of these advisories, the background indoor air results may not fully represent “typical” indoor air in situations where residents have not been so advised.

This report has been prepared using the assumption that all 1,1-DCE in indoor air at the site is derived from a groundwater source. However other background studies indicate that measurable concentrations of DCE in indoor air do occur at residences far from this site. In addition, the potential for formation of DCE from degradation of household products rich in 1,1,1-TCA is poorly known. The true population distribution of background 1,1-DCE is not fully known but may be determined with further investigation.

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